



D E C L A R A T I O N

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This 22nd day of June, 2007

A handwritten signature in cursive script, reading "S. Kawasaki", written over a horizontal line.

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[DOCUMENT NAME] Claims

[Claim 1] A secondary battery comprising: a positive electrode; a negative electrode; and a porous film layer that is integrally formed on a surface of at least one of said positive electrode or said negative electrode, said porous film layer being composed mainly of a fine particulate filler,

wherein said particulate filler comprises a joined-particle filler that is in the form of a plurality of primary particles that are joined and bonded to one another.

[Claim 2] The secondary battery in accordance with claim 1, wherein said form of being joined and bonded to one another is such that said primary particles are partially melted and bonded together due to a heat treatment.

[Claim 3] The secondary battery in accordance with claim 1, wherein said joined-particle filler comprises a metal oxide.

[Claim 4] The secondary battery in accordance with claim 1, wherein said particulate filler comprises: a joined-particle filler comprising a metal oxide; and resin fine particles.

[Claim 5] The secondary battery in accordance

with claim 1, wherein said porous film layer contains a binder, and said binder comprises a binder comprising a polyacrylic acid derivative.

[Claim 6] The secondary battery in accordance with claim 1, wherein said secondary battery is a lithium ion secondary battery comprising: a positive electrode comprising a composite lithium oxide; a negative electrode comprising a material capable of retaining lithium; and an electrolyte comprising a non-aqueous solvent.

[Claim 7] The secondary battery in accordance with any one of claims 1 to 6, further comprising a separator that is independent of said positive electrode and said negative electrode.

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(Translation)

[DOCUMENT NAME] Specification

[TITLE OF THE INVENTION] Secondary battery

[Technical Field]

[0001]

The present invention relates to a secondary battery having excellent discharge characteristics, and, more particularly, to a porous film layer that is formed on an electrode plate as a protective layer.

[Background Art]

[0002]

Secondary batteries, for example, chemical batteries such as lithium ion secondary batteries, typically include an electrode group composed of a positive electrode, a negative electrode, and a separator that electrically insulates the electrode plates while holding an electrolyte.

With respect to the above-mentioned electrode plates, there has recently been proposed an electrode plate integrated with a porous film, which is prepared by applying a dispersion slurry containing a filler and a resin binder onto the surface of an electrode plate and drying it with hot air to form a porous film, in order to improve product quality (see Patent Document 1).

Also, there has been proposed a separator

comprising a polyolefin resin and an inorganic powder (see Patent Document 2).

A porous film is usually prepared by mixing a particulate filler and a resin binder with a solvent and forming a porous film slurry by using a dispersing device. The particulate filler material used therein is supplied in powder form. Conventionally, it is more specifically in the form of powdery particles composed mainly of spherical primary particles that gather by weak van der Waals forces (cohesion) since they are fine particles. FIG. 3 shows a schematic view of a non-joined-particle filler 2 composed mainly of spherical primary particles.

Thus, such particles are dispersed into the form of primary particles as evenly as possible by means of a dispersing device such as a bead mill, in order to stabilize the thickness and porosity of the resulting porous film (e.g., see Patent Document 3).

[Patent Document 1] Japanese Patent Publication
No. 3371301

[Patent Document 2] Japanese Laid-Open Patent
Publication No. Hei. 10-50287

[Patent Document 3] Japanese Laid-Open Patent
Publication No. Hei. 10-106530 (FIG. 2)

[Disclosure of the Invention]

[Problem that the Invention Is to Solve]

[0003]

However, in the case of a conventional porous film composed of a filler that is dispersed into the form of primary particles, fine particles are filled into the porous film at high densities due to dispersion, so that the value of the porosity, which represents the volume ratio of space in the porous film, becomes low. It has been found that due to the low value, charge/discharge characteristics at a high rate degrade and charge/discharge in a low temperature environment becomes impossible.

For example, according to the above-mentioned method of using an electrode plate integrated with a porous film, which is prepared by applying a dispersion slurry containing a filler and a resin binder onto the surface of an electrode plate and drying it with hot air to form a porous film, short-circuits and the like are reduced when a battery assembly is formed during production. However, the charge/discharge characteristics of the battery degrade and, in particular, when the battery is charged/discharged at a relatively large current, for example, when cellular phones or notebook computers may be used in environments at temperatures of 0°C or lower, the characteristics remarkably degrade, which poses a large practical problem.

The present invention relates to highly safe secondary batteries including an electrode plate that has a porous film on the surface thereof and intends to provide a battery capable of discharging at a large current

particularly at low temperatures.

[Means for Solving the Problem]

[0004]

In order to solve the above-mentioned problems, the present inventors have conducted diligent study and made the following inventions.

[0005]

The secondary battery of the present invention is a secondary battery including: a positive electrode; a negative electrode; and a porous film layer that is integrally formed on a surface of at least one of the positive electrode and the negative electrode. The porous film layer comprises a particulate filler and a binder. The particulate filler comprises a joined-particle filler that is in the form of a plurality of primary particles joined and bonded to one another.

[0006]

In this way, by using joined particles in the form of a plurality of primary particles that are joined and bonded to one another as the particular filler, which is a material of the porous film, it is possible to significantly improve charge/discharge characteristics at a large current, which has been a problem to be solved.

[0007]

The present invention uses joined particles in the form of a plurality of primary particles that are

joined and bonded to one another, instead of a particulate filler material in the form of agglomerated primary particles that gather by van der Waals forces or dry-joining and that easily become separated into primary particles by the above-mentioned dispersing process. This configuration enables easy formation of a porous film having an incomparably high porosity.

[0008]

When joined particles comprising a plurality of primary particles joined and bonded to one another are used as a filler, the filler is prevented from being filled into a porous film at high densities because of the interaction of the three-dimensionally-joined structure of the filler. Probably for this reason, the formation of a porous film with a porosity incomparably higher than a conventional one becomes possible.

[0009]

As described above, when a battery is produced by using a porous-film-integrated electrode plate that has a high-porosity porous film on the electrode plate, the conventional problems such as large-current charge/discharge and low-temperature-environment charge/discharge characteristics can be solved.

[0010]

Also, the joined particles used are supposed to be subjected to a strong shearing force by a dispersing

device that is used to prepare a slurry in a production process. Hence, when primary particles are partially melted and bonded together due to a heat treatment, such form of being joined and bonded together provides stable porosity and is thus preferable.

[Effects of the Invention]

[0011]

As described above, the present invention can realize a secondary battery that is excellent in low-temperature discharge characteristics and safety and provide a method for producing secondary batteries at low costs.

[Best Mode for Carrying Out the Invention]

[0012]

Preferable embodiments of the present invention are hereinafter described.

[0013]

The invention as recited in claim 1 of the present invention is directed to a secondary battery including: a positive electrode; a negative electrode; and a porous film layer that is integrally formed on a surface of at least one of the positive electrode and the negative electrode. The porous film layer is composed mainly of a particulate filler. The particulate filler comprises a joined-particle filler that is in the form of a plurality of primary particles that are joined and bonded to one

another.

[0014]

The present invention relates not only to lithium ion secondary batteries but also to secondary batteries such as alkaline storage batteries. In these secondary batteries, among the characteristics of batteries made with an electrode plate having a porous film, it is known that behavior at a large current and at low temperatures, for example, 0 °C 3C discharge characteristics depend on the porosity of the porous film. Thus, in this embodiment, the effects of the present invention are described in terms of "porosity".

[0015]

The measurement of porosity is performed, for example, as follows.

[0016]

A dendrite-like particulate filler comprising a plurality of primary particles bonded to one another is mixed with a binder in a solvent and dispersed in a bead mill. The mixture is then passed through a filter with a suitable mesh size, to obtain a porous film paste. This paste is applied onto a metal foil with a doctor blade so as to achieve a predetermined thickness, to obtain a test sample, and the porosity of the applied film is calculated. In this calculation, the porosity of the porous film portion of the test sample is determined by first measuring

the weight and thickness of the porous film, calculating the volume of the solid portion from the true density of the filler, the true density of the binder, and the mixing ratio thereof, and dividing it by the volume of the whole porous film to obtain a volume ratio.

[0017]

In the case of using the conventional particulate filler that easily becomes separated into primary particles, almost all such porous films have low porosities of 45% or less, and it is difficult to achieve a higher porosity. In this case, the 0 °C 3C discharge characteristics of, for example, lithium ion secondary batteries were not satisfactory.

[0018]

Contrary to this, in the case of using a joined-particle filler 1 comprising a plurality of joined particles of the present invention, as illustrated in FIG. 1, the porosity easily becomes 45% or higher. A porous film comprising such a joined-particle filler exhibits similarly high porosity even when titanium oxide, alumina, zirconia, tungsten oxide or the like is used as the material of the particles.

[0019]

Further, in various battery systems requiring a porous film layer, the present invention is also effective in applications where the porosity needs to be controlled

as appropriate, and is believed to be a technique that can heighten porosity, which has been particularly difficult to achieve.

[0020]

Also, when the present invention is a lithium ion secondary battery, if the size of primary particles of the joined particles used in the present invention is too large, there is a problem in that a short-circuit may occur during experimental battery production. Thus, the maximum particle size of the primary particles is preferably 3 μm or less.

[0021]

The maximum particle size can be determined, for example, by using a wet laser particle size distribution analyzer manufactured by Microtrack Inc. Since the primary particles are made of a substantially homogeneous substance, there is almost no difference between volume basis and weight basis in particle size distribution measurement. Thus, the maximum particle size can be regarded as the volume- or weight- basis 99% value (D_{99}) in particle size distribution measurement.

[0022]

Also, in the case of using joined particles with a primary particle size of more than 3 μm , the sedimentation of particles in a dispersion slurry is promoted. As a result, for example, prevention of short

circuits of, for example, lithium ion secondary batteries becomes difficult.

[0023]

Further, when the present invention is a lithium ion secondary battery, if the particle size of the joined particles used in the present invention is too large, the following problem arises during experimental battery production. When a porous film of 20 μm or less, which is usually a design requirement, is formed by application, large particles are caught, for example, by the application blade of a blade coater, so that streaks are likely to occur, thereby resulting in a significant decrease in yields. Thus, the mean particle size of the joined-particle filler is desirably 10 μm or less. If it is more than twice, the operational advantage of the present invention is exhibited markedly, which is preferable.

[0024]

The mean particle size of the joined-particle filler can be determined, for example, by using a wet laser particle size distribution analyzer manufactured by Microtrack Inc, in the same manner as in the case of primary particles. Since the primary particles are made of a substantially homogeneous substance, there is almost no difference between volume basis and weight basis in particle size distribution measurement. Thus, the mean particle size can be regarded as the 50% value (D_{50}).

[0025]

In most lithium ion secondary batteries, the practical thickness of the porous film based on battery design is 20 μm or less. The porous film is applied onto the electrode plate by a die nozzle method, a blade method, or the like. If the size of the joined-particle filler exceeds 10 μm , even in the case of forming a porous film with a thickness of 20 μm , for example, by a blade method, agglomerated particles are caught in the gap between the electrode plate surface and the blade tip, so that streaks occur, thereby resulting in a decrease in yields of porous films. Hence, in view of the production process of the porous film, the size of the joined-particle filler is more desirably 10 μm or less.

[0026]

The invention as recited in claim 2 of the present invention pertains to the secondary battery as recited in claim 1, where the form of being joined and bonded to one another is such that the primary particles are partially melted and bonded together due to a heat treatment.

[0027]

In order to examine the methods of joining and bonding, agglomerated particles were prepared by utilizing mechanical shearing force and agglomerated particles were prepared by utilizing a binder. However, in both cases,

they became separated in a dispersing device used to prepare a slurry and it was confirmed that they returned to primary particles. Contrary to this, the joined particles prepared by a joining method utilizing heating are more desirable because they do not become separated even when they are subjected to, for example, a bead mill dispersing process, which is a common dispersing process.

[0028]

The invention as recited in claim 3 of the present invention relates to the secondary battery as recited in claim 1, where the joined-particle filler comprises a metal oxide.

[0029]

When metal particles are used to form joined particles instead of a metal oxide, the control of the heating atmosphere becomes difficult and the cost increases. Also, when they are applied to batteries, battery design becomes difficult unless careful consideration is given to oxidation reduction potential; for example, metal particles are dissolved in an electrolyte and further deposited on electrodes as dendrites, which can cause a short-circuit. When resin fine particles are used to form joined particles, it is difficult to achieve practical manufacturing costs and practical manufacturing amounts. Thus, a metal oxide is most desirable from the industrial viewpoint.

[0030]

The invention as recited in claim 4 of the present invention pertains to the secondary battery as recited in claim 1, where the particulate filler comprises: a joined-particle filler comprising a metal oxide; and resin fine particles.

[0031]

In forming a porous film using the joined-particle filler of the present invention, it is also possible to use resin fine particles such as polyethylene fine particles as part of the particulate filler, if necessary. Since resin fine particles have a specific gravity of approximately 1.1 and are more lightweight than metal oxides having a specific gravity of around 4, they are effective in reducing the weight of batteries.

[0032]

The invention as recited in claim 5 of the present invention relates to the secondary battery as recited in claim 1, where the porous film layer contains a binder and the binder comprises a binder comprising a polyacrylic acid derivative.

[0033]

Currently, in secondary batteries such as alkaline storage batteries and lithium ion secondary batteries, batteries with a wound structure are predominant, and electrode plates and the like need to be flexible in order to have such a wound structure.

[0034]

A highly flexible porous film can be realized by using a polyacrylic acid derivative as the binder. It is effective to use the polyacrylic acid derivative of the present invention as the binder in order to provide a wound-structure battery having the widest industrial applicability.

[0035]

The secondary battery as recited in claim 6 of the present invention is a lithium ion secondary battery including: a positive electrode comprising a composite lithium oxide; a negative electrode comprising a material capable of retaining lithium; and an electrolyte comprising a non-aqueous solvent.

[0036]

When the secondary battery of the present invention is a lithium ion secondary battery, the present invention is most effective. It is believed that the present invention can play a large role in this filed with a large market size, since it can have a large effect on the performance and quality of products in the market.

[0037]

The lithium ion secondary battery of the present invention uses the following organic electrolytes, so it is basic to assure sufficient safety design. The porous film using the joined-particle filler of the present invention

can provide the battery with excellent heat resistance and heat stability and can therefore be of great value.

[0038]

With respect to the positive electrode plate of the lithium ion secondary battery employed to describe the present invention, composite oxides such as lithium cobaltate and modified materials thereof (e.g., eutectic material containing aluminum or magnesium), lithium nickelate and modified materials thereof (e.g., part of the nickel is replaced with cobalt), and lithium manganate and modified materials thereof may be used as the active material.

[0039]

With respect to the negative electrode, various natural graphites, various artificial graphites, silicon composite materials, and various alloy materials may be used as the active material.

[0040]

With respect to the electrolyte, various lithium compounds such as LiPF_6 and LiBF_4 may be used as the salt. Also, ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) may be used as the solvent singly or in combination. Also, in order to form a good film on the positive and negative electrodes and ensure stability upon overcharge, it is also possible to use a small amount of an additive such as

vinylene carbonate (VC) or cyclohexyl benzene (CHB).

[0041]

In a lithium ion secondary battery not using a conventional resin separator, which is one mode of the present invention, it is also possible to realize a battery with excellent performance by integrally forming the porous film comprising the joined particles of the present invention on the electrode plate. Since the present invention eliminates the need to use a conventional resin separator, it is possible to realize a low-cost battery.

[0042]

However, of course, inclusion of foreign matter in the manufacturing process causes a problem of short-circuits, and it is thus necessary to take sufficient preventive measures such as introduction of a clean process.

[0043]

The secondary battery as recited in claim 7 is directed to the secondary battery as recited in any one of claims 1 to 6, which has a separator that is independent of the positive electrode and the negative electrode.

[0044]

The separator is not particularly limited if it has a composition capable of withstanding the operating range of the lithium ion secondary battery; however, it is common to use a micro-porous film made of olefin resin, such as polyethylene or polypropylene, singly or in

combination. The separator allows an improvement in prevention of a short-circuit, so that safety and reliability are enhanced.

[Example 1]

[0045]

An Example of the present invention is hereinafter described, but the following description is merely indicative of one example and the present invention is not to be limited to the description. In the description of this example, alumina is used as an example of the filler material and a lithium ion secondary battery is used as an example of the battery system.

[0046]

A joined-particle filler was prepared as follows. A raw material powder comprising alumina primary particles with a mean particle size of $0.1\ \mu\text{m}$ were sintered at 1100°C for 20 minutes, and the size was adjusted in a wet ball mill using 15-mm alumina balls to obtain a joined-particle filler with a mean particle size of $0.5\ \mu\text{m}$. 100 parts by weight of the joined filler, 4 parts by weight of a polyacrylic acid derivative binder, and an N-methylpyrrolidone solvent were mixed together with a stirring device such that the nonvolatile component content was 60% by weight. Thereafter, this mixture was dispersed in a bead mill with an internal volume of 0.6 L containing 0.2-mm-diameter zirconia beads at 80% of the internal volume.

In this way, a porous film paste was obtained. This paste of Example is designated as a paste A1.

[0047]

The paste A1 was applied onto a metal foil with a doctor blade such that the thickness was approximately 20 μm , to obtain a test sample. The porosity of the porous film portion of this test sample was determined by measuring the weight and thickness of the porous film, calculating the volume of the solid portion from the true density of the filler, the true density of the binder, and the mixing ratio thereof, and dividing it by the volume of the whole porous film to obtain a volume ratio.

[0048]

FIG. 2 shows a scanning microscope photo (SEM photo) of the test sample of the paste A1. It can be seen that the joined-particle filler 1 forms large pores and that the porosity is high.

[0049]

Further, a porous film paste was prepared in the same manner as the paste A1 except for the use of primary particles of titanium oxide with a mean particle size of 0.2 μm as the raw material powder, and the porosity was measured in the same manner. This paste of Example is designated as a paste A2.

[0050]

For comparison, a porous film paste was prepared

in the same manner as the paste A1 except for the use of a fine particulate filler of $0.5\ \mu\text{m}$ instead of the joined-particle filler, and the porosity was measured in the same manner. This paste of Comparative Example is designated as a paste B1.

[0051]

FIG. 4 shows an SEM photo of the test sample of the paste B1. It can be seen that the non-joined-particle filler 2 cannot form large pores and that the porosity is not high.

[0052]

Further, for comparison, alumina primary particles with a mean particle size of $0.1\ \mu\text{m}$ were used as the raw material powder, and a mechanical shearing force was applied thereto by a vibration mill equipped with a 40-mm-diameter alumina bar to obtain an agglomerated-particle filler with a mean particle size of $0.5\ \mu\text{m}$. A porous film paste was prepared in the same manner as the paste A1 except for the use of the agglomerated-particle filler instead of the joined-particle filler of the paste A1, and the porosity was measured in the same manner. This paste of Comparative Example is designated as a paste B2.

[0053]

Also, alumina primary particles with a mean particle size of $0.1\ \mu\text{m}$ were mixed with 4% by weight of a PVDF binder, to obtain an agglomerated-particle filler with

a mean particle size of $0.5 \mu\text{m}$. A porous film paste was prepared in the same manner as the paste A1 except for the use of the agglomerated-particle filler instead of the joined-particle filler of the paste A1, and the porosity was measured in the same manner. This paste of Comparative Example is designated as a paste B3.

[0054]

The results are shown in (Table 1).

[0055]

[Table 1]

| Paste | Filler used | Primary particle size (μm) | Secondary particle size (μm) | Porosity (vol%) |
|----------|---|---|---|-----------------|
| Paste A1 | Almina joined particles | 0.1 | 0.5 | 60 |
| Paste A2 | Titanium oxide joined particles | 0.1 | 0.5 | 58 |
| Paste B1 | Alumina fine particles | 0.5 | 0.5 | 44 |
| Paste B2 | Alumina agglomerated particles (vibration mill) | 0.1 | 0.5 | 45 |
| Paste B3 | Alumina agglomerated particles (binder) | 0.1 | 0.5 | 44 |

[0056]

It was found that the joined-particle fillers of the present invention clearly exhibited high porosity values. It was also confirmed that the joined particles of titanium oxide exhibited a high porosity, and the effects

of the present invention were confirmed in this example.

[0057]

As the comparative examples, the agglomerated particles were prepared by applying the mechanical shearing force with the vibration mill or the like and the agglomerated particles were prepared by using the binder. However, in both cases, the porosity was low and a qualitative analysis by a scanning electron microscope confirmed that the agglomerated particles returned to primary particles. This is probably because the joined particles of Comparative Examples became separated due to the shearing force applied in the dispersing device to prepare the slurry.

[0058]

Contrary to this, the joined particles of the paste A1 prepared by the joining process utilizing heating in the Example of the present invention did not become separated even when subjected to, for example, the bead mill dispersing process, which is a common dispersing process, and exhibited a high porosity. It was thus found that the present invention was clearly effective.

[0059]

(Evaluation of battery)

In order to evaluate battery charge/discharge characteristics, batteries were experimentally produced by using the paste A1, A2, or B1 to form a porous film on the

negative electrode, and the effectiveness of the present invention was tested.

[0060]

The porous film was formed on a negative electrode plate hoop which was prepared as follows. The following describes the methods for producing the negative electrode plate and the positive electrode plate used in the experimental battery production.

[0061]

For forming the negative electrode plate, 3 kg of artificial graphite, a rubber particulate binder composed of a styrene-butadiene copolymer, CMC, and a suitable amount of water were stirred with a double-arm kneader, to form a negative electrode paste. This paste was applied onto a 10- μm thick copper foil and then dried, to obtain a negative electrode hoop. This applied hoop was roll-pressed such that the total thickness was 180 μm and the active material layer density was 1.4 g/cm³, to obtain a pressed negative electrode hoop.

[0062]

The positive electrode plate was prepared as follows. Lithium cobaltate, PVDF, acetylene black, and a suitable amount of NMP were stirred with a double-arm kneader, to form a positive electrode paste. This paste was applied onto a 15- μm thick aluminum foil, which was then dried and rolled such that the total thickness was

160 μm and the active material layer density was 3.3 g/cm³. Thereafter, this was slit to a width such that it was capable of being inserted into a cylindrical type 18650, to obtain a positive electrode hoop.

[0063]

The above-mentioned porous film paste was applied onto the above-mentioned negative electrode plate hoop such that the film thickness was 5 μm when dried, and the hoop was cut into the shape of the electrode plate of the cylindrical battery.

[0064]

The positive electrode plate and the negative electrode plate integrated with the porous film were wound with a 15- μm thick resin separator interposed therebetween, to form a group. This group was inserted into the cylindrical battery can, and 5 g of an electrolyte prepared by dissolving 1M LiPF₆ and 3% by weight of VC in a solvent mixture of EC/DMC/EMC was injected therein. In this way, batteries A1, A2 and B1 were experimentally produced. These batteries had a design capacity of 2000 mAh.

[0065]

The following describes the method for evaluating the batteries used in the Example.

[0066]

The sealed, completed batteries (non-defective items free from chipping, cracks, or separation due to

winding) were preliminarily charged and discharged twice and stored in a 45°C environment for 7 days. Thereafter, they were charged and discharged in a 20°C environment as follows.

(1) Constant current discharge: 400 mA (cut-off voltage 3 V)

(2) Constant current charge: 1400 mA (cut-off voltage 4.2 V)

(3) Constant voltage charge: 4.2 V (cut-off current 100 mA)

(4) Constant current discharge: 400 mA (cut-off voltage 3 V)

(5) Constant current charge: 1400 mA (cut-off voltage 4.2 V)

(6) Constant voltage charge: 4.2 V (cut-off current 100 mA)

Next, after 3-hour stand-by, they were charged and discharged in a 0°C environment as follows.

(7) Constant current discharge: 6000 mA (cut-off voltage 3 V)

[0067]

The capacities obtained were defined as 0°C-3C discharge characteristics.

[0068]

Also, Table 2 summarizes the performance of the assembled batteries.

[0069]

[Table 2]

| Paste | Filler used | Discharge characteristics 0°C-3C discharge (mAh) |
|----------|---------------------------------|--|
| Paste A1 | Alumina joined particles | 1700 |
| Paste A2 | Titanium oxide joined particles | 1200 |
| Paste B1 | Alumina fine particles | 500 |

[0070]

These results indicate that Example 1 exhibits high porosities and excellent low-temperature discharge characteristics. Comparative Example 1 with the porous film composed of the non-joined particle filler clearly had a low porosity and low low-temperature large-current discharge characteristics.

[Example 2]

[0071]

Joined fine particles were prepared by applying a heat treatment to alumina particles composed mainly of primary particles with particle sizes of 0.1 μm to 5 μm , and porous film slurries were prepared in the same manner as the above.

[0072]

In order to form a stable porous film, the paste needs to be so stable that sedimentation and the like do

not occur, for example, for several days, since the prepared paste is subjected to a process such as filter refinement. If a large amount of a binder is used, stabilization is possible. However, as a result of examination, it was found that the degree of sedimentation is dependent on the particle size in a system with a practical composition, for example, a system containing 4 parts by weight of a binder per 100 parts by weight of a filler. When a joined-particle filler comprising particles of 3 μm or less is used, still-standing sedimentation stability was 4 days or more. A porous film paste using a joined-particle filler comprising primary particles of 4 μm or more exhibited still-standing sedimentation stability of within 1 day, which was low.

[Example 3]

[0073]

Alumina particles with a primary particle size of 0.2 μm were heat treated in the same manner to obtain joined particles. Thereafter, using a ball mill containing 3-mm-diameter alumina balls at 30% of the internal volume thereof, a suitable amount of water and the alumina particles subjected to the heat joining treatment were placed therein, followed by a wet crushing process. Joined-particle fillers with mean particle sizes of 0.3 μm to 30 μm were prepared by changing the operation time of the ball mill. They were dispersed by the above-mentioned

method to obtain porous film slurries. Each slurry was applied onto a negative electrode plate with a most commonly used blade coater. The intended thickness was 20 μm . As a result, when the mean particle size of the joined particles was 10 μm or less, the formation of an applied film was possible. However, when the joined particles of larger than 10 μm were used to form the slurry, the occurrence of streaks was high and on an unpractical level. Of course, taking counter measures is not completely impossible, for example, by applying a filter refinement process more sufficiently or broadening the gap between the electrode plate and the blade. However, since such special measures can cause confusion to manufacturing sites and increase costs, they should be avoided. In this sense, when the mean particle size of the joined particles was 10 μm or less, desirable results were obtained.

[Example 4]

[0074]

Taking the most common lithium ion battery as an example, the common structure is a cylindrical battery obtained by winding sheet-like electrode plates into a cylindrical shape or a prismatic battery obtained by winding them into the form of an elliptically cylindrical shape. Since the porous film of the present invention is also formed on an electrode plate, it is wound as described

above. At this time, if the porous film layer is hard, problems such as cracking or separation of the porous film occur.

[0075]

A porous film was prepared by adding 4 parts by weight of polyvinylidene fluoride PVDF to 100 parts by weight of a joined-particle filler with a mean particle size of 0.5 μ m. Cylindrical batteries were produced, and the short-circuit incidence thereof was 10%, which was abnormally high. In the experimental production of common ion batteries, the short-circuit incidence is 0.5% or less. When the short-circuited experimental batteries were disassembled, their porous films were found to have many cracks, which were remarkable particularly near the center of the winding.

[0076]

Contrary to this, in experimental batteries having porous films made with a flexible rubber binder of a polyacrylic acid derivative, the short-circuit incidence was 0.5% or less. When they were disassembled, no cracking was found on the porous film surface, probably because the flexible rubber binder of the polyacrylic acid derivative made the porous film highly flexible, thereby making it possible to avoid cracking.

[Example 5]

[0077]

The following describes an Example in which a battery does not have a resin separator. Using the porous film paste as described in the foregoing Example 1, a porous film of 20 μm was formed on a negative electrode hoop. This was laminated with a positive electrode plate, and the laminate was wound to form a group without using a resin separator. In this way, an experimental battery was produced. This battery exhibited 1650 mAh, which means its low temperature characteristics are as good as an experimental battery that was produced by using a 15 μm resin separator and a hybrid electrode plate having a 0.5 μm porous film on a negative electrode plate. Because there is no need to use a conventional expensive resin separator, low cost battery production becomes possible, which is regarded as being of great industrial value.

[Industrial applicability]

[0078]

The secondary battery of the present invention is useful as a highly safe power source for portable and other devices.

[BRIEF EXPLANATION OF THE DRAWINGS]

[0079]

[FIG.1] A schematic view of a joined-particle filler of the present invention;

[FIG. 2] An SEM photo of a test sample according to one example of the present invention;

[FIG. 3] A schematic view of a conventional non-joined particle filler; and

[FIG. 4] An SEM photo of a conventional test sample according to one comparative example.

[Explanation of Reference Numerals]

[0080]

1 Joined-particle filler

2 Non-joined-particle filler



2004-041106

(Translation)

[DOCUMENT NAME] Abstract

[ABSTRACT]

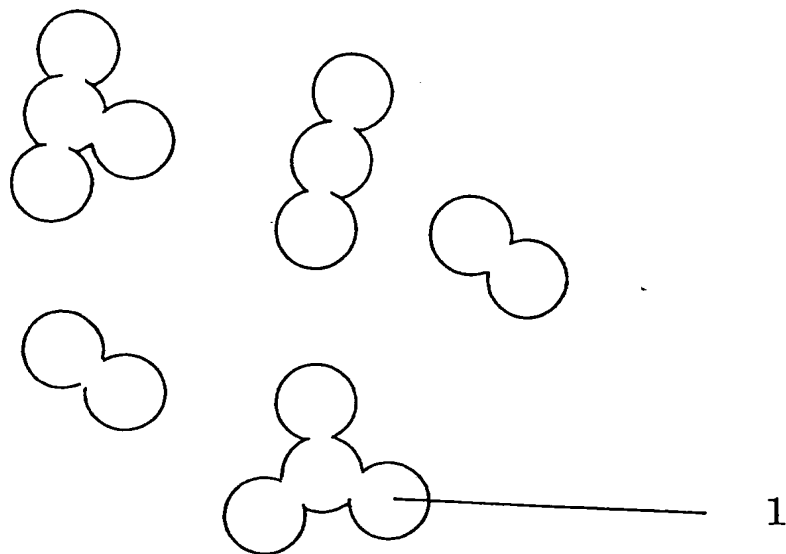
[OBJECTIVE] In a highly safe secondary battery including an electrode plate that has a porous film on the surface thereof, a battery capable of discharging at a large current particularly at low temperatures is provided.

[SOLVING MEANS] Provided is a secondary battery that includes: a positive electrode; a negative electrode; and a porous film layer that is integrally formed on a surface of at least one of the positive electrode and the negative electrode. The porous film layer includes: a particulate filler including a joined-particle filler in the form of a plurality of primary particles that are joined and bonded to one another; and a binder. This secondary battery has a high porosity, so that it is capable of discharging at a large current at low temperatures, which is regarded as being particularly important from the practical point of view.

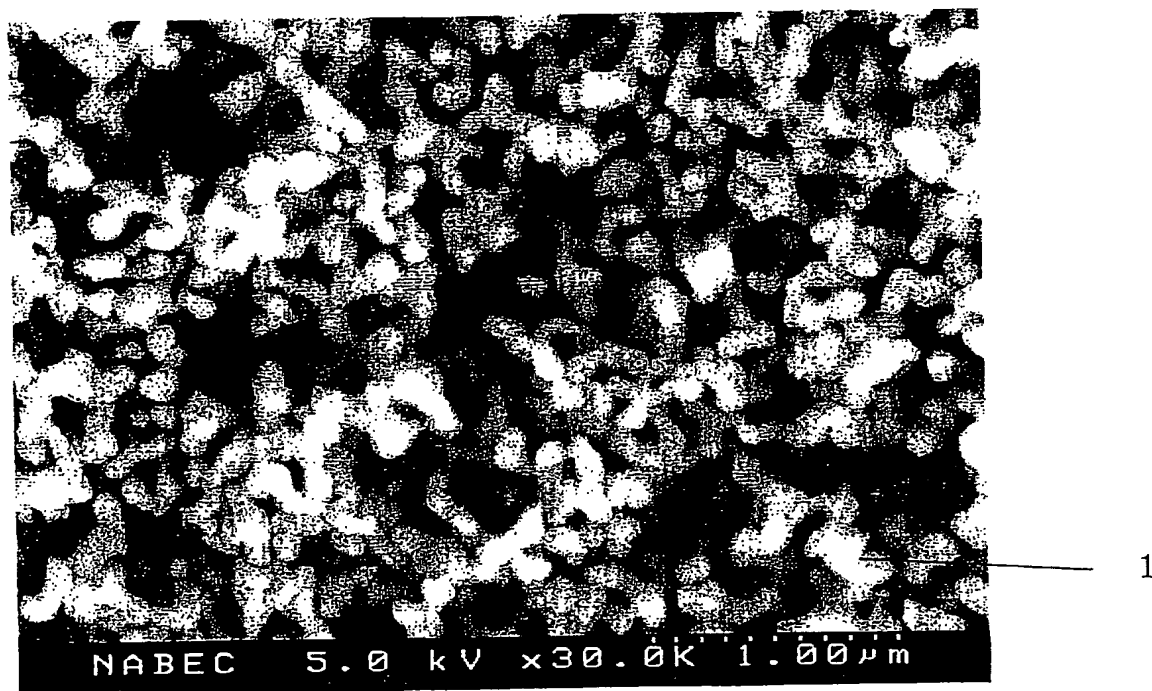
[SELECTED DRAWING] FIG. 1

【書類名】図面 [DOCUMENT NAME] Drawings

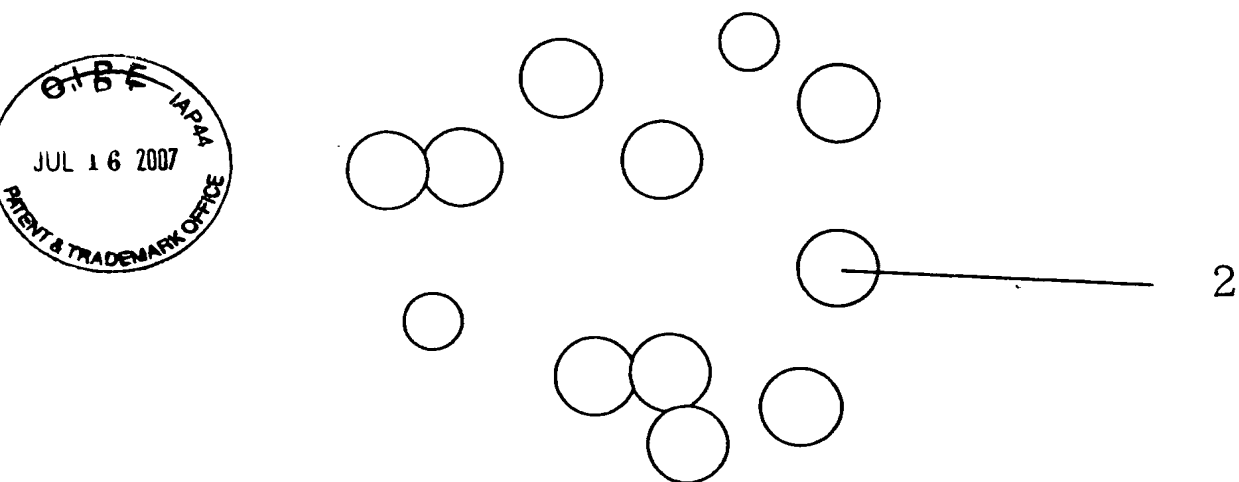
【図1】[FIG. 1]



【図2】[FIG. 2]



【図 3】 [FIG. 3]



【図 4】 [FIG. 4]

